

EVALUATION OF NEW TYPE OF CHEMICAL PRE-TREATMENT APPLIED ON LOW-CARBON STEEL SUBSTRATE USING SEM AND EDS ANALYSIS

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Abstract: The article is focused on evaluation of the chemical pre-treatments applied on steel substrate using the electron microscope. The most important aim of chemical pre-treatment is the removal of contaminants, corrosion products etc. from the material surface and obtaining such a basic material surface, which will provide sufficient corrosion resistance of the base material and suitable conditions for adhesion of paints or other finish coatings to steel material. The paper focuses on the evaluation of chemical pre-treatments excluded on low-carbon steel sheet using SEM and EDS analysis. The carbon steel sheet had excluded coatings of chemical pre-treatments (Fe phosphate, coating based on nanotechnology) and the character of excluded layers on an electron microscope at different magnifications has been studied. Nanotechnology based product is a technology, which can in the future replace the classical phosphating process because it should provide better corrosion resistance of pre-treated materials (as the producer states). These products create the nanolayer on the material surface which is created by sol-gel technology. The main goal of our research is testing of this product and comparing with the Fe phosphating process. It is a part of extensive research.

Keywords: chemical pre-treatment, phosphating, nanopassivation, steel substrate, SEM, EDS.

Introduction

Chemical pre-treatments of the surface are used to remove the impurities from the material surface, to increase the corrosion resistance and also contribute to better adhesion of the coating to the base material. For example, during the phosphating process exclusion of the crystalline layer of phosphates occurs, which improves the adhesion of the applied coating [1]. When selecting the method of surface chemical pre-treatment of the base material, it should be considered whether the degree of preparation provides the required level of cleanliness of the surface and also the surface roughness and surface profile for the coating to be applied to the base material. Good adhesion for the coating to the base material is the first step to ensure good corrosion resistance of the coated product. Although phosphating creates suitable conditions for the adhesion of the coating, it is an effort to remove it from the production process and replace it with a more suitable alternative. The reasons for removing of phosphating are several. We can name, for example: high energetic severity of the phosphating technological process, because phosphating is performed at elevated temperature (dipping application of phosphate 50-70 °C, spraying application of phosphate 40-60 °C); production of sewage sludge, which is necessary to liquidate etc. [2; 3]. Suitable replacement of the phosphating process could be chemical products based on nanotechnology – nanolayers. These are multimetallic products based on organosilanes, which ensure better adhesion of the coating system and increase the corrosion resistance [4-7]. In addition to it, these nanolayers work in the room temperatures and are ecological, so in the future it seems like the alternative replacement of the classical phosphating.

Within the experiment the product Alfipas 7816 was tested. It is a product which is the result of efforts to develop a technology that would meet the ecological requirements and simultaneously would provide to metallic materials good corrosion resistance comparable to traditional methods of chemical surface preparation such as chromate, ferric or zinc phosphate. As reported by literature [8], the product Alfipas 7816 (ENVIROX “ENVIROX SG”) is based on hexafluorozirkon acid (H_2ZrF_6). This product contains a zirconium complex with six fluorine atoms, a fluoride and a polymeric component (polyacrylic acid or phenolic resin). Into products sometimes elements that contain Cu and Si are also added, which in this product (like resin) increase conversion coating resistance to corrosion and increase the adhesion of the coating applied to the surface of the material after chemical pre-treatment [3; 8].

Creating of this coating on the surface of the material is done by the sol-gel technology. This method is based on the synthesis and stabilization of the nanoparticles. The sol-gel technology is used to prepare the oxidic coatings and is based on dissolution of the organometallic compounds in a suitable solvent and subsequent hydrolysis, which is directed to the condensation and polymerization system to form a gel [1; 2; 4]. The quantity, shape and size of the nanoparticles are determined by a

number of parameters of solution - pH, temperature, stabilizers, excipients, concentration of precursor – of the chemicals that are involved in the chemical reactions, e.g., metal alkoxides. On the surface of metal creation of the stabilization cover occurs, which protects it against corrosion. References [1; 2] state that the coating material provides temporary protection for storage. The conversion coating is formed by particles of zirconium, which are formed in the form of zirconium oxide on the substrate surface. The coating thickness reaches tens of nanometers (≈ 30 nm). References [4; 5; 7] suggested that the corrosion resistance of the coating is comparable to that of zinc and iron phosphate (thickness of ≈ 250 nm) [7; 8].

Currently, the influence of nanopassivating layers on the final quality of powder coated steel materials is not yet fully explored. Our research could provide to the firms in practice a basis when deciding whether to stay at the surface pre-treatment method, which uses conventional technologies with pre-treatment phosphating + nanopassivation to ensure maximum corrosion resistance of painted parts, whether or feel free to move only to nanotechnology without loss of corrosion resistance of thus pre-treated parts.

The article deals with the observation and exploration of individual layers formed on the surface of the experimental samples (alkaline degreasing + nanopassivation / Alk + Zr; iron phosphating + nanopassivation / Feph + Zr; alkaline degreasing + iron phosphate + nanopassivation / Alk + Feph + Zr) using SEM and EDS analysis.

Preparation of the experimental samples

The experimental samples were prepared by the following schemes of chemical pre-treatment of the surface as follows:

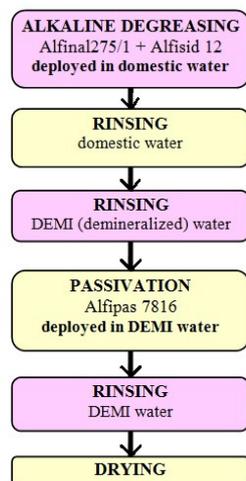


Fig. 1. Scheme of the sample chemical pre-treatment variant 1 (Alk+Zr, sample A)

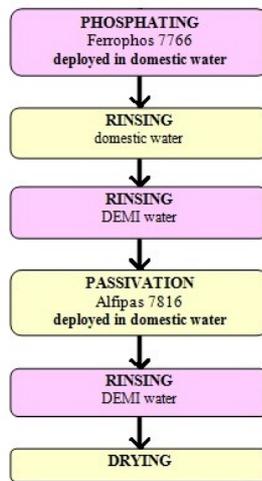


Fig. 2. Scheme of the sample chemical pre-treatment variant 2 (Feph+Zr, sample B)

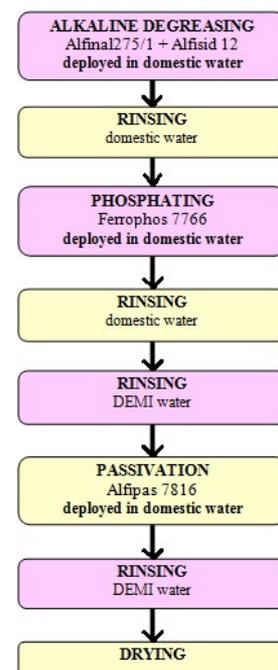


Fig. 3. Scheme of the sample chemical pre-treatment variant 3 (Alk+Feph+Zr, sample C)

SEM and EDS analysis of excluded coatings of chemical pre-treatment

For evaluation of excluded coatings of chemical pre-treatment and their connection with the base material a scanning electron microscope TESCAN VEGA 3 was used. We have tested three variants of experimental samples – variant 1 (alkaline degreasing + Zr nanopassivation), variant 2 (Fe phosphate + Zr nanopassivation), variant 3 (alkaline degreasing + Fe phosphate + Zr nanopassivation). All three procedures (variant 1 -3) were tested in the form of lacquered sheets before

evaluating in the corrosion chamber with salt spray. It is a part of extensive research in which we are testing the corrosion resistance of powder lacquered low carbon unalloyed steel sheets. It was expected that the nanotechnology product in combination with alkaline degreasing (variant 1) will have better results than the combination in variants 2 and 3. The best results after corrosion load in the corrosion chamber had the variant 3 [9-11]. We decided to try to find the cause of this effect. To this goal we used SEM and EDS analysis which helps find the differences between the excluded layers, helps study the character of these layers and find the elements which are the basic for creating of the layers.

SEM analysis

The following figures show the documentation from the electron microscope I received from the analysis of the surface of each sample and next comparing of the excluded layers of individual samples.

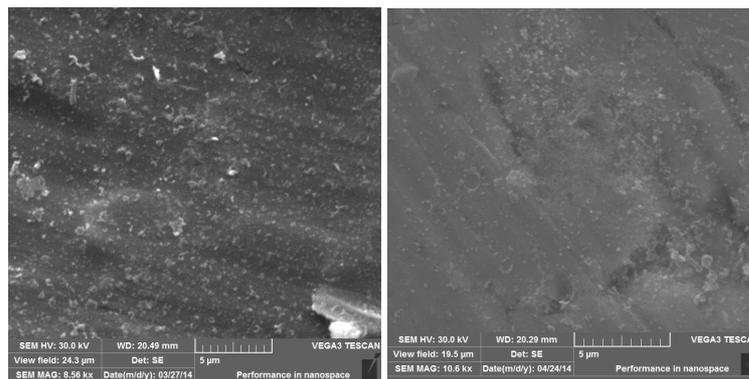


Fig. 4. Surface sample A – variant 1

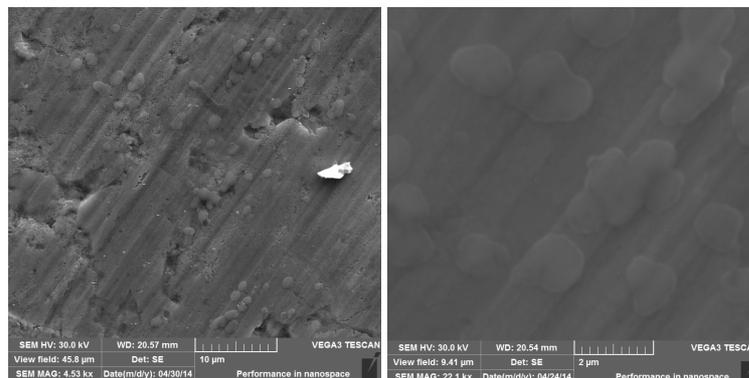


Fig. 5. Surface sample B – variant 2

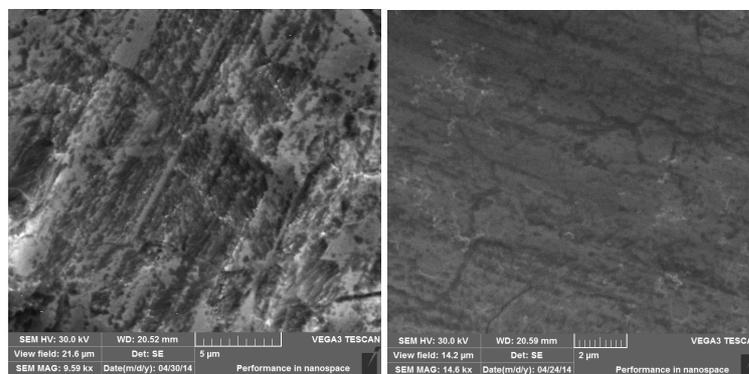


Fig. 6. Surface sample C – variant 3

The figures show that it is possible to observe differences in the exclusion of individual pre-treatment (A - Alk + Zr, B - Feph Zr + C - Alk Feph + Zr).

Sample A has chemical pre-treatment alkaline degreasing + nanopassivation Alfipas 7816. This type of pre-treatment is excluded on the surface material in the form of particles covering the whole surface of the material. The surface was highly reactive after application of the chemical pre-treatment and after drying. It reacted in several minutes in the air in the laboratory environment and on the surface of the material surface corrosion began to form. As we can see from the figures, on the surface of the sample material oxides are apparent (Fig. 4, white particles).

For sample B with chemical pre-treatment Fe phosphate + nanopassivation Alfipas 7816 we noticed a difference in the excluded chemical pre-treatment. On the surface of the sample larger particles of spherical shape were excluded, other than is the case with the previous sample.

Sample C with chemical pre-treatment alkaline degreasing + Fe phosphate + nanopassivation Alfipas 7816 has a completely different character of the layer. The excluded coating is not in particulate form on the surface of the material, but the compact layer, which is broken with cracks. On the surface of the samples with this type of chemical pre-treatment, there were observed no particles or needles phosphate.

EDS analysis

For EDS analysis the Bruker analyser was used. EDS analysis is carried out in the depth 1 - 3 µm into the material surface, so in these dimensions our excluded protecting layers are included.

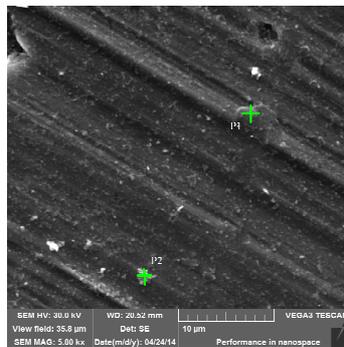


Fig. 7. Sample surface A point EDS analysis (P1, P2)

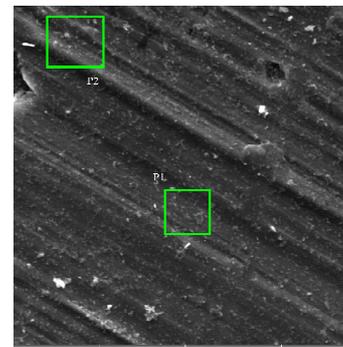


Fig. 8. Sample surface A EDS analysis (S1, S2)

Table 1

EDS analysis of the sample A – variant 1

Analysed elements	P1	P2	S1	S2
O, wt. %	5.47	3.07	2.85	3.34
Zr, wt. %	0.79	0.54	0.92	0.86
Si, wt. %	0.21	0.13	0.08	0.10
F, wt. %	3.39	3.43	4.12	3.69

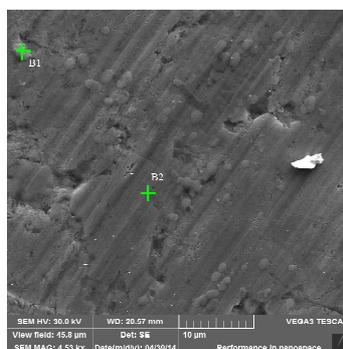


Fig. 9. Sample surface B point EDS analysis (P1, P2)

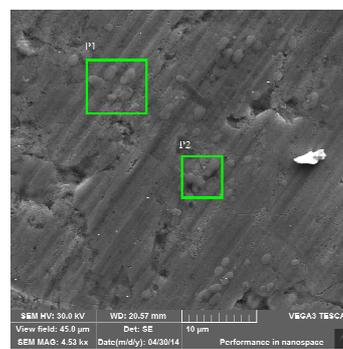


Fig. 10. Sample surface B EDS analysis (S1, S2)

Table 2

EDS analysis of the sample B – variant 2

Analysed elements	P1	P2	S1	S2
O, wt. %	2.73	2.22	4.20	5.21
Zr, wt. %	0.77	0.75	2.04	0.52
Si, wt. %	0.01	0.06	0.06	0.11
F, wt. %	3.90	3.99	3.40	2.77

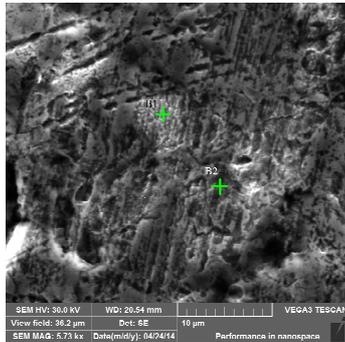


Fig. 11. Sample surface C point EDS analysis (P1, P2)

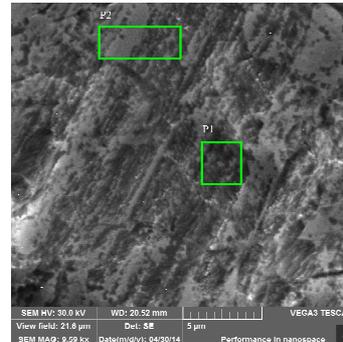


Fig. 12. Sample surface C EDS analysis (S1, S2)

Table 3

EDS analysis of the sample C – variant 3

Analysed elements	B1	B2	P1	P2
O, wt. %	2.43	7.12	4.14	10.49
Zr, wt. %	0.71	0.41	0.51	0.83
Si, wt. %	0.04	0.14	0.03	0.07
F, wt. %	3.56	3.55	3.32	3.28

Conclusions

The paper deals with evaluation of excluded coatings of various chemical pre-treatment types using SEM and EDS analysis. In this evaluation different types of chemical pre-treatment were observed (variant 1-3). Chemical pre-treatment Alk + Zr was excluded in the form of small particles (Fig. 4, 7, 8) when these particles uniformly cover the surface of the material and form clusters. The pre-treatment Feph + Zr (Fig. 5, 9, 10) has a surface layer of material different character. There is a layer formed by spherical bodies free of particulate matter. Phosphate is like closed with nanopassivation and spherical particles having a size of a few microns (the smallest particles about 1 micron largest to 4 mm). The third type of surface preparation Alk + Feph + Zr created on the surface of the material has again a completely different structure from the other two types of pre-treatment. This pre-treatment resulted in the effect the sol-gel technology. The sol-gel technology forming layers on the surface of the material after oven drying (samples dried at 130°C) cause cracking of the conversion protective layer. These cracks are visible on the surface of the samples in Fig. 6, 11, 12. Cracks can cause reduction of the protective effect conversion layer against corrosion. Even if we take into account the possibility that the protective layer by variant 3 is breached by cracks, its corrosion protection is greater than by variant 1 and 2, because it is a protective layer which covers the entire surface of the material.

With EDS analysis the occurrence of particular elements that each chemical pre-treatment contains was documented, therefore by nanopassivation Zr, F, Si and O and P for phosphate. From the measurement of the concentration of elements on excluded layers of chemical pre-treatment we can say that the content of elements forming a protective layer of chemical pre-treatment is very low and it corresponds to the corrosion resistance of thus pre-treated samples, especially in the case of chemical pre-treatment Alk + Zr. These samples begin in a laboratory environment after oven drying very quickly react with the surrounding environment and cover with a layer of corrosion products.

We think that the use of zirconium nanopassivation Alfipas 7816 in the form in which it was tested, it is not practical for use in enterprises without the use of phosphates appropriate. Despite the advantages that come with this nanotechnology, the phosphating technology is still preferable especially in higher corrosion resistance and thus increases the life of the pre-treated materials. Nanotechnological product Alfipas 7816 is then particularly suited as a sealant for phosphate which pores are sealed and phosphate may result in increasing the corrosion resistance of phosphated materials. After the performed analyses we can say that the best result for good corrosion resistance has the variant 3 which is created with alkaline degreasing, iron phosphating and nanopassivation. In the next research we will focus on the nanopassivation improvement and influencing of the chemical composition of this chemical in the interest of better corrosion protection of the pretreated materials.

References

1. Philip A., Schweitzer P.E. *Paint and Coatings: Applications and Corrosion Resistance*. Corrosion Technology – Edition 23. Taylor&Francis, 2005, 672 p., ISBN 1574447025.
2. Chou T. P., Chandrasekaran C., Limmer S., Nguyen C., Cao G. Z. Organic-inorganic sol-gel rating for corrosion protection of stainless steel. *Journal of Materials Science, Letters* 21, 2002, pp. 251-255, ISSN 0261-8028.
3. Materne T., Buyl F., Witucki G. L. *Organosilane Technology in Coating Applications: Review and Perspectives*. [online] [25.7.2012]. Available at: <http://www.dowcorning.com/content/publishedlit/26-1402-01.pdf>.
4. Voevodin A. A., Shtansky D. V., Levashov E., A., Moore J. J. *Nanostructured Thin Films and Nanodispersion Strengthened Coatings*. Springer, 2004, Nato Science Series II: - Edition 155, ISBN 1-4020-2221-2.
5. Cavaleiro A., Hosson J. T. *Nanostructured Coatings, Nanostructure Science and Technology*. Springer, 2006, 648 p, ISBN 0-387-25642-3.
6. Adhikari S., Unocic K. A., Zhai Y., Frankel G. S., Zimmerman J. *Fristad Hexafluorozirconic acid based surface pretreatments: Characterization and performance assessment*. *Electrochimica Acta*, 2011, Vol. 56, No. 4, pp. 1912-1924 [online] [1.7.2013]. Available at: <http://www.science-direct.com/science/article/pii/S0013468610009692>.
7. Kuśmierczak S., Michna Š. *Analýza korozního poškození povrchu hliníkových materiálů dlouhodobým skladováním*. *Strojírenská technologie*, 2011, Vol. 4, No. 4, pp. 32-36, ISSN 1211-4162.
8. Ndreata F. *Development and industrial scale-up of ZrO₂ coatings and hybrid organic-inorganic coatings used as pre-treatments before painting aluminium alloys*. *Progress in Organic Coatings*, 2011, Vol. 72, No. 1-2. [online] [16.4.2013]. Available at: <http://www.sciencedirect.com/science/article/pii/S0300944011000294>.
9. Svobodová J., Kuśmierczak S. *Analýza poškození práškově lakované vrstvy po korozním zatížení*. *Strojírenská technologie*, 2014, Vol. XIX, No 2, pp. 119-125, ISSN 1211-4162.
10. Kuśmierczak S., Svobodová J. *Microscopic Evaluation of Protective Coating by Coated Sheets after Corrosion Load*. *Manufacturing Technology, Journal for Science, Research and Production*, December 2012, Vol. 12, No. 13, pp. 151-157, ISSN 1213-2489.
11. Kusmierczak S., Naprstkova N., Svobodová J. *Evaluation of sheet degradation with surface treatment*. *Engineering for Rural Development* 11, pp. 32-36, 2012, ISSN 1691-3043.